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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The binding of halide ions by host <u>1</u> (1,8-dichloro-1,8-distanna-bicyclo[6.6.6]eicosane) in solution have been studied by NMR spectroscopy. In CDCl ₃ solutions, host <u>1</u> maintains its structural integrity in the presence of tetraalkylammonium halides. Host <u>1</u> shows no binding properties towards chloride, bromide or iodide ions. The binding constant of host <u>1</u> for chloride must be less than 0.003 M ⁻¹ at 30°C whereas the binding constant for the acyclic model tributyltin chloride is 20 M ⁻¹ . However, as predicted by models and the X-ray crystal structure of <u>1</u> , this host binds fluoride ion strongly, presumably within its cavity; the binding constant at 30 °C is 100-200 M ⁻¹ which is comparable to that of the acyclic model. Thus, the selectivity for binding fluoride over other halide ions is at least 5.5 kcal/mol. The 1-F ⁻ complex was readily observed in both ¹¹⁹ Sn and ¹⁹ F NMR spectroscopy; both techniques gave a ¹¹⁹ Sn- ¹⁹ F coupling constant of ca 100 Hz. The rate constants for complexation --decomplexation are small (k<100 s ⁻¹).					
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Macrocycles Containing Tin.

A Small, Exclusive Host for the Fluoride Ion

by

Martin Newcomb* and Michael T. Blanda

Department of Chemistry
Texas A&M University
College Station, Texas 77843

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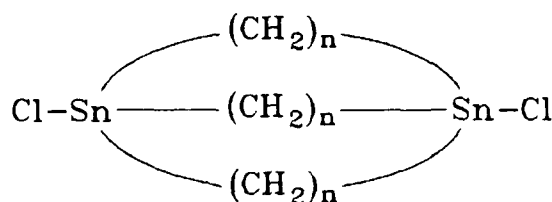
Department of Chemistry
Texas A&M University
College Station, Texas 77843

✓ **Abstract:** The binding of halide ions by host 1 (1,8-dichloro-1,8-distanna-Ni²⁺, *Macrocyclic* bicyclo[6.6.6]eicosane) in solution have been studied by ¹(NMR) spectroscopy. In CDCl₃ solutions, host 1 maintains its structural integrity in the presence of tetraalkylammonium halides. Host 1 shows no binding properties towards chloride, bromide or iodide ions. The binding constant of host 1 for chloride must be less than 0.003 M⁻¹ at 30 °C whereas the binding constant for the acyclic model tributyltin chloride is 20 M⁻¹. However, as predicted by models and the X-ray crystal structure of 1, this host binds fluoride ion strongly, presumably within its cavity; the binding constant at 30 °C is 100-200 M⁻¹ which is comparable to that of the acyclic model. Thus, the selectivity for binding fluoride over other halide ions is at least 5.5 kcal/mol. The 1-F⁻ complex was readily observed in both ¹¹⁹Sn and ¹⁹F NMR spectroscopy; both techniques gave a ¹¹⁹Sn-¹⁹F coupling constant of ca 1100 Hz. The rate constants for complexation--decomplexation are small ($k < 100 \text{ s}^{-1}$).

MACROCYCLES CONTAINING TIN.

A SMALL, EXCLUSIVE HOST FOR THE FLUORIDE ION

Molecular recognition of anionic guests by multidentate, Lewis acidic hosts in organic media has been observed in only limited cases.¹ Further, neutral, macrocyclic receptors for anions or bases have just begun to receive attention.^{2,3} We recently reported the synthesis and chloride anion binding properties of a series of Lewis acidic macrobicyclic hosts (1-4) containing bridgehead tin atoms.³ Hosts 2 and 3 bound chloride more strongly than host 4, presumably reflecting a better "fit" of the chloride ion in the cavities of 2 and 3; thus, size selectivity in the binding of chloride was demonstrated. The behavior of host 1 in the presence of chloride was perhaps more noteworthy since this species showed no apparent complexation with chloride.⁽³⁾



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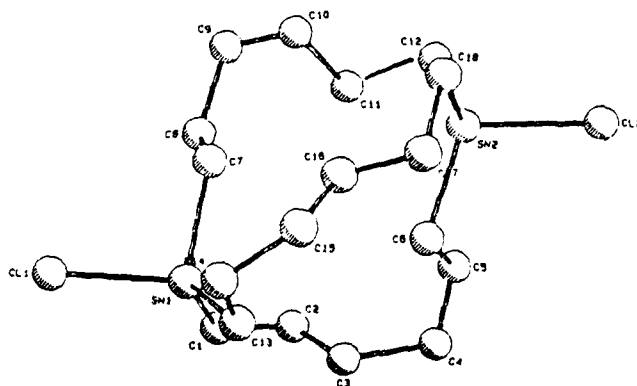


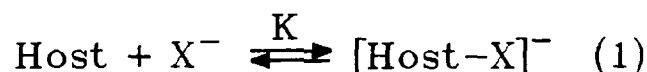
Figure 1. X-ray crystal structure of 1.

In this communication we report further studies of the interesting host 1.⁴ This compound was found to be Lewis acidic exclusively towards the small fluoride anion which it complexed strongly; it exhibited no Lewis acidic properties towards other halide ions. The remarkable binding selectivity of 1 and the apparent stability of the tin-chlorine bonds in 1 in the presence of other halides support our conclusion³ that hosts 1-4 complex halide ions by inclusion within the cavity.

For the series of hosts 1-4, molecular models had suggested the possibility of inclusion of chloride into the cavities of 2-4 but not into that of 1. An X-ray crystal structure of 1 confirmed the prediction of the models (Figure 1).⁵ In the solid state, the molecule is a crude sphere with a tin-tin distance of 5.25 Å. Assuming a tin atom radius of 1.4 Å,⁶ the chloride ion (diameter ca. 3.6 Å)⁶ should not fit between the tin atoms, but inclusion of the fluoride anion (diameter ca. 2.6 Å)⁶ might be expected.

The binding properties of the tin-containing hosts in solution are conveniently studied by ¹¹⁹Sn NMR spectroscopy since tin species typically experience about a 200 ppm upfield chemical shift upon conversion from a four-coordinate stannane to a pentavalent stannate.⁷ Careful NMR^{8a} studies of the

potential binding of chloride by 1 were performed to confirm of our earlier observation. When solutions of host 1 in CDCl_3 were treated with tetrahexylammonium chloride, the ^{119}Sn signal from 1 at δ 148.5 remained sharp and unshifted. Ultimately, solutions containing a five-fold excess of chloride (0.41 M) were studied. Spectra were recorded at 30 and -50 °C to guarantee that at least one set of studies was performed outside of the range of dynamic NMR behavior. From the 30 °C spectra, assuming the fast exchange limit, the amount of complexed host 1 was less than 0.5%, and the binding constant for Eq 1 must be less than 0.003 M^{-1} . From the -50 °C spectra (signal to noise = 50:1), assuming the slow exchange limit, the amount of complex (expected at δ 0-30³) was less than 2%, and K_{eq} must be less than 0.01 M^{-1} . For comparison, host 2 binds chloride strongly under these conditions ($K_{\text{eq}} = 20\text{-}50 \text{ M}^{-1}$)³; the reduction in cavity size from 2 to 1 leads to a reduction in binding energy of chloride of at least 3.7 (-50 °C) or 5.5 (30 °C) kcal/mol.



Similar behavior was observed in the ^{119}Sn NMR spectra of CDCl_3 solutions of 1 containing 0.41 M bromide and 0.41 M iodide. As expected, the signal from 1 was unaffected in its chemical shift and line-shape showing that there was no detectable binding of these halides. When these solutions were allowed to stand for two days, the ^{119}Sn from 1 remained unchanged indicating that the tin-chlorine bond in 1 was stable over this time period. In simple mono-halo tin compounds, the tin-halogen bonds are labile.⁹

Dramatically different behavior was observed in the ^{119}Sn NMR spectra of 1 in the presence of tetrabutylammonium fluoride. Upon addition of increments of the fluoride salt, the signal from uncomplexed 1 at δ 148.5 was reduced in intensity and a new doublet centered at δ -6.5, with a ^{119}Sn - ^{19}F coupling constant of 1090 (\pm 50) Hz, was observed. Figure 2 shows spectra of 1 containing about 0.4 and 0.5 equivalents of fluoride per mole of host. It is noteworthy that the ^{119}Sn NMR spectra were unchanged upon standing for several days at room temperature; specifically, there was no new signal in the region of the uncomplexed host. This shows that host 1 maintained its structural identity, and the fluoride ions did not replace chloride despite the rapid complexation--decomplexation.

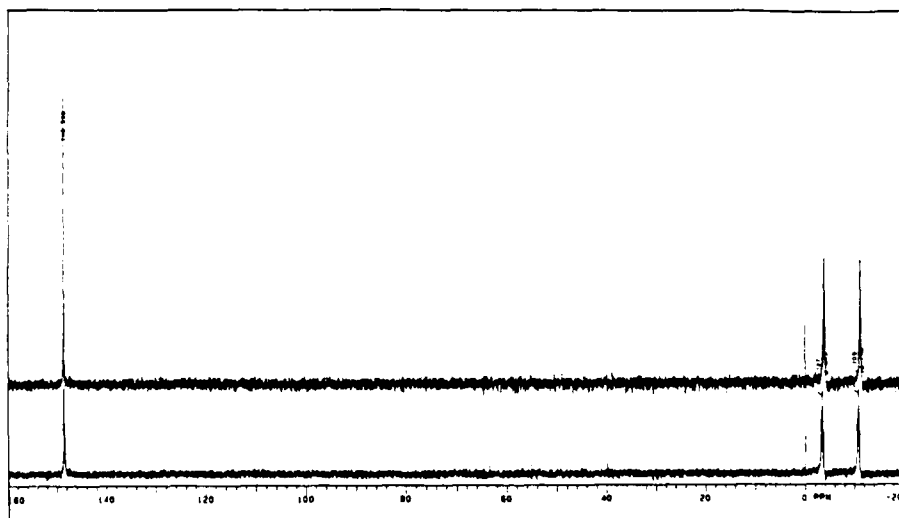


Figure 2. ^{119}Sn NMR spectra in CDCl_3 of 1 with 0.4 (lower) and 0.5 (upper) equivalents of tetrabutylammonium fluoride.

For comparisons to a simple model, the ^{119}Sn NMR spectra of mixtures of tributyltin chloride (5) and tetrabutylammonium fluoride were studied. Since the halogens are freely exchanging under these conditions, the identity of the tin species cannot be rigorously assigned, but qualitative conclusions are warranted. Upon incremental additions of the fluoride salt to a CDCl_3 solution of 5, the signal (initially at δ 156) remained sharp but shifted smoothly upfield. With ca 2 equivalents of fluoride present, the signal was at δ -30.7 although this did not appear to be the final limiting chemical shift.

The host 1-F^- complex could also be observed by ^{19}F NMR spectroscopy.^{8b} A solution containing ionic fluoride shows a very broad signal centered at δ -88.6. In the presence of limiting host 1, the ^{19}F spectrum was complex, containing three significant sets of sharp peaks. A signal at δ -76.1 was readily assigned to the 1-F^- complex based on the ^{119}Sn and ^{117}Sn satellites with coupling constants of ca 1100 Hz. A signal at δ -89.1 was assigned to free fluoride, and a signal at δ -75.5 was not assigned.

Since sharp NMR peaks were observed in the slow exchange limit for the host 1-F^- complex at 30 °C in the ^{119}Sn spectra, limiting values for the rate constants for complexation can be calculated. Line-shape analysis¹⁰ showed that the (presumed) first-order rate of decomplexation (k_r) must be less than 100 s^{-1} based on the signals for the free and complexed host in the ^{119}Sn spectrum and the sharp doublet signals of the complex. In contrast, the rate constant for exchange in binding of model 5 to fluoride must be greater than $8 \times 10^5\text{ s}^{-1}$ based on the observed fast exchange in the NMR spectra of 5--fluoride mixtures.

Despite the substantial reduction in the rates of complexation-decomplexation of fluoride by host 1, which we attribute to steric interactions involving the hydrocarbon rings, the binding constant remained high. Using the

^{119}Sn and ^{19}F spectra of one sample of **1** and fluoride, the ratio of complexed to free species for both host and fluoride were determined. The binding constant at 30 °C was 100 or 200 M^{-1} depending upon the assignment of the fluoride signal at δ -75.5. Thus, host **1** binds F^- at least five orders of magnitude more strongly than it binds chloride or, apparently, any other donor. The impressive binding selectivity of host **1** is more apparent when one compares these results with those for the acyclic model **5**. For **5**--fluoride mixtures, the binding constant at 30 °C was ca 220 M^{-1} , similar to that for **1**. The binding constant for **5** with chloride ion, however, is also large (20 M^{-1}).¹²

There is a striking parallel between our observations with the macrocyclic Lewis acidic hosts **1-4** and the cation binding properties of their basic counterparts, the well-studied crown ethers, cryptands etc. Specifically, the proper fit of a guest within the cavity of the host can lead to selective complexation such as we observed in the binding of chloride by **2-4**, but substantially greater size-selective effects exist when a small guest fits a cavity and its larger homologues are excluded. Thus, in its binding of fluoride, host **1** resembles, for example, small-cavity, lithium- and sodium-specific spherands reported by Cram.¹⁴ We expect that other properties of the cation-binding hosts will also be paralleled by anion binding hosts.

Acknowledgment. We thank the Office of Naval Research for financial support.

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4. The systematic name for **1** is 1,8-dichloro-1,8-distannabicyclo[6.6.6]-eicosane.
5. Full details of the molecular structure of **1** and other hosts will be submitted for publication.
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8. (a) ^{119}Sn NMR spectra were obtained on a Varian XL-200 (74.6 MHz) or a Varian XL-400 (149.2 MHz) spectrometer with gated proton decoupling; chemical shifts are reported in ppm downfield from external Me_4Sn . (b) ^{19}F NMR spectra were obtained on a Varian XL-400 spectrometer at 376 MHz; chemical shifts are reported in ppm relative to external 1,1,1-trifluorotoluene

9. For a discussion of halogen exchange in trialkyltin halides, see: Van Der Kelen, G. P.; Van Den Berghe, E. V.; Verdonck, L. in *Organotin Compounds*, Vol. 1; Sawyer, A. K., ed.; Marcel Dekker: New York, 1971. Halogen exchange on a mono-halo tin might proceed by either a back-side S_N2 mechanism or a front-side pseudo-rotation mechanism, but the structure of 1 apparently precludes either mechanism.
10. A two-site exchange model¹¹ was used. The T_2 values used were 0.1 s; for the objective of determining the onset of line broadening, the T_2 values are relatively unimportant.
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12. The binding constants for "5" with fluoride and chloride were estimated from experimentally measured ^{119}Sn NMR spectra of mixtures of 5 with the halides which were in fast exchange.¹³ The method also gave calculated chemical shifts for the fully complexed species that were in the expected range (δ -53 for F^- and δ -62 for Cl^-).
13. A simple computer program was written which used the double-reciprocal (Hildebrand-Benesi) treatment as modified for NMR data in the fast exchange limit (see: Connors, K. A. *Binding Constants, The Measurement of Molecular Complex Stability*, Wiley-Interscience: New York, 1971). The program solved for the binding constant by a least squares calculation then re-calculated the concentration of guest and iterated. Typically, the program converged after 5-10 iterations.
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Dr. M. F. Hawthorne
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Professor O. T. Beachley
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Dr. W. Hatfield
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